Oxygen gettering in Si by He ion implantation-induced cavity layer

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Abstract Oxygen gettering in Si by the He induced cavity layer was investigated in this work. A cavity layer was generated in Si sample by He implantation and annealing. The morphology of the cavity layer depending on the dose of He and the annealing temperature was presented in the paper. This cavity layer may serve as an efficient oxygen gettering layer during the high temperature oxidation process and accumulate the oxygen from the annealing atmosphere as well as the implanted oxygen. The phenomenon gives the idea that the cavity layer can be employed to define the oxide formation in Si and further to facilitate the formation of the buried oxide layer (BOX) in Si aiming at the Si-on-Insulator (SOI) structure fabrication. The oxygen gettering ability of the cavity layer in Si was investigated by cross section transmission electron microscopy and auger electron spectroscopy.

Key words Implantation, Gettering, SIMOX, Precipitate

1 Introduction

Gettering is an important process for accumulation of an extrinsic impurity from a device region to pre-defined gettering sites. Cavity formation under the surface of a silicon wafer by helium or hydrogen ion implantation has been well established as an efficient method to trap impurities, such as interstitial Ni, Au, Cu, Co, Pt, Fe and Si atoms[1–4]. The chemisorptions of the implanted species, as the cavity surface containing highly reactive dangling bonds, leads to the reduced impurity concentration in the active area of the device.

In this work, oxygen gettering effect in the cavity layer induced by He ion implantation was investigated, so as to form an oxygen gettering layer at the early stage of Separation by IMplanted OXygen (SIMOX), a technology for fabricating Silicon On Insulator (SOI) substrates by high dose implanting of oxygen and high temperature annealing[5]. In order to reduce the oxygen dose, which is necessary for the formation of a continuous buried oxide layer, accumulation of the implanted oxygen into a narrow layer is critical at early stage of the process.

In conventional low dose SIMOX process, the Internal Thermal Oxidation (ITOX) process was developed to increase the thickness of the pre-formed Buried OXide (BOX) layer and improve the physical and electrical quality of the Si/SiO_2 interface of SIMOX wafer[6,7]. ITOX precedes further growth of the formed BOX layer by gettering the oxygen from high temperature oxidation process under an oxygen-enriched atmosphere (10% higher). Some oxygen atoms reaching the Si/SiO_2 interface may penetrate into the superficial Si surface layer, being gettered by the upper Si/SiO_2 interface of the BOX layer.

Efficiency of oxygen-gettering in normal ITOX process, however, is limited to the amount of in-diffused oxygen and processing time[6,7]. In this paper, oxygen gettering by cavity layer from the annealing atmosphere in high temperature oxidation process was studied. The gettering behaviours of oxygen in cavity layer, and the implanted oxygen, were investigated by Auger electron spectroscopy (AES) and cross-sectional transmission electron microscopy (XTEM).

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2 Experimental

Five samples were prepared as shown in Table 1. The samples were implanted with 45 keV He^+ ions to the doses of $4\times10^{16}/cm^2$ or $8\times10^{16}/cm^2$. A pre-annealing was preformed to form the cavity layer in the sample. Then three of them had been implanted with 200 keV oxygen to the dose of $5\times10^{16}/cm^2$, while the window dose required to form a continuous BOX layer in low dose SIMOX process is around $7\times10^{17}/cm^2$[8,9]. Therefore, a layer of insulated SiO_2 precipitates instead of a planar BOX layer forms during the high temperature oxidation process. One Si sample implanted with the same dose oxygen was used as the control (Sample O). Finally, the samples were annealed at 1300℃ for 3 h in an atmosphere of $Ar:O_2$=100:20.

Table 1 Parameters of the cavity layer formed in Si sample*

Samples	He dose / 10^{16} cm^{-2}	Pre-annealing (for 1 h) Temperature / ℃
CL1O	4	1000
CL1	4	1000
CL2O	8	1000
CL2	8	1000
CL3O	4	900

* CL1, CL2 and CL3 stand for the three cavity layers formed by different processes, and O indicates that the samples had been implanted with 200 keV oxygen to 5×10^{16} cm^{-2}.

3 Results and discussion

TEM images of the samples (Fig.1) show morphology of the cavity layer induced by the He implantation. Thickness of the layer, size distributions of the cavities and the cavity density in the layer are dependent on the He implantation dose and the annealing temperature. Figs.1a, b and c illustrate that, as the temperature increases from 900℃ to 1100℃, thickness of the cavity layer reduces from 138 nm to 77 nm and number fraction of the big cavities increase, whereas the cavity density decreases. The cavity layer thickness and mean size of the cavities in the layer increase dramatically in Figs.1d and e, where the samples were implanted with $8\times10^{16}/cm^2$ of the He ions. The small cavities in the layer generally have a spherical shape, while the large cavities are faceted along {111}, {100} and {110} due to their lower surface free energy. The reduced cavity layer thickness of the samples annealed at higher temperatures is resulted from dissolution of the small cavities formed predominantly at edges of the cavity layer due to the Oswald ripening mechanism[10,11]. The released vacancies either are annihilated on the surface or move to the nearby larger cavities. The cavity migration and coalescence lead to the cavity coarsening[12]. Therefore, the large cavities are frequently found in the centre of the cavity layer where the original vacancy concentration had its maximum value.

Fig.2a shows the oxygen profiles of the samples after a high temperature oxidation process. The oxygen gettered in the cavity layer (CL-peak) is located at the depth around 480 nm, and the implanted oxygen (R_p-peak) is located at the depth around 640 nm. Both of the peaks are observed in the oxygen profile of samples CL1O and CL3O. With increased He dose for the cavity layer formation, as in Sample CL2O, the implanted oxygen is completely gettered by the cavity layer. Fig.2b shows the retained amount of oxygen as calculated by integrating the corresponding peaks of the oxygen profiles shown in Fig.2a. For Sample O, the shape of oxygen profile is different, and the amount of oxygen at R_p is reduced in comparison to the He-implanted samples. This indicates some out-diffusion of oxygen.

For the He-implanted samples, the measured total amount of oxygen is higher than the as-implanted oxygen dose. It seems that the He implantation activates the in-diffusion of oxygen during oxidation. For Sample CL1O, the amount of oxygen at the R_p peak is approximately equal to that of Sample O and to the oxygen amount in the CL-peak of Sample CL1 without oxygen implantation. This indicates that the oxygen in CL-peak of Sample CL1O is meanly gettered from the annealing atmosphere. The oxygen accumulation at the R_p-peak vanishes in Sample CL2O, whereas the oxygen amount around CL-peak increases significantly over the retained oxygen in Sample O. This can also be attributed to the additional incorporation of oxygen by in-diffusion from the annealing atmosphere. The higher He dose of Sample CL2 dose not significantly enhances the amount of oxygen in comparison to Sample CL1. The oxygen gettering in Samples CL3O and CL3 are slightly less than that in the Samples CL1O and CL1.

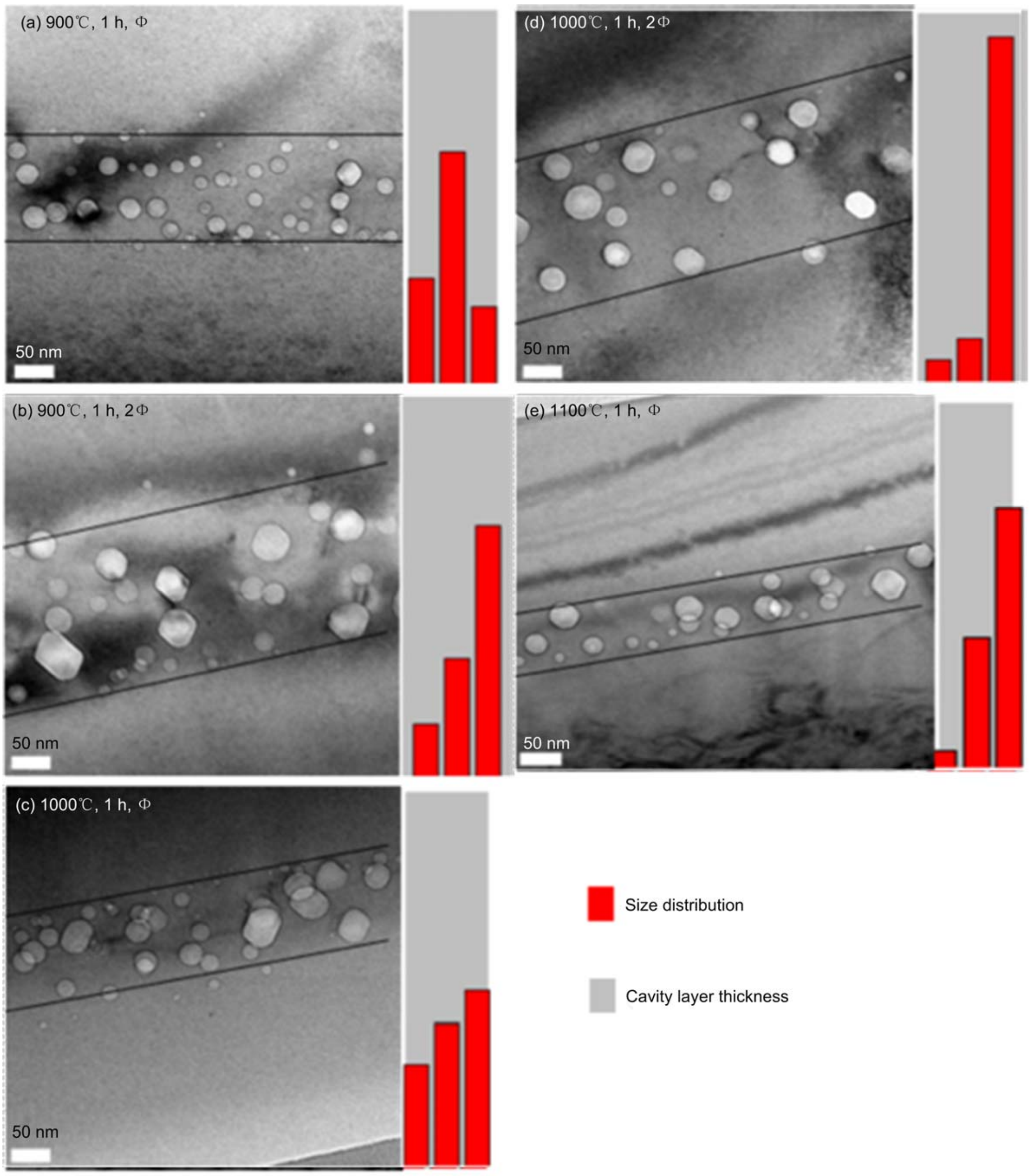

Fig.1 XTEM images of the cavity layer in silicon samples implanted with 45 keV He ions to different doses. There is no O implantation in these samples. This figure only shows the cavity layer. And annealed at different temperatures. (a), (c) and (e) implanted with 4×10^{16} cm^{-2} (Φ) He ions and annealed at 900, 1000 and 1100℃, respectively, for 1 hour, (b) and (d) implanted with $8\times10^{16}/cm^{/2}$ (2Φ) He ions and annealed at 900 and 1000℃, respectively, for 1 hour. The red columns from the left to right side represent the relative fraction of the small, medium and large cavities in the layer, and the width of the grey rectangle illustrates the thickness of the cavity layer.

The XTEM images of the buried SiO_2 precipitates in the samples are shown in Fig.3. The SiO_2 precipitates are located in double layers in Samples CLO1 (Fig.3a) and CLO3 (Fig.3c) and in a single layer in Sample CLO2 (Fig.3b). The depth of SiO_2 precipitate layer shown in Sample CL1 (Fig.3d) is consistent with the depth of the upper SiO_2 precipitate layer in Sample CLO1 (Fig.3a), but the precipitate density in Sample CL1 (Fig.3d) is much lower. In Samples CLO2 (Fig.3b) and CL2 (Fig.3e) of higher dose He implantation, average sizes of the SiO_2 precipitates are larger.

Fig.4 shows XTEM imagestaken from a thicker area of the XTEM specimen in Fig.3. The images also show the dislocations that connect the CL-layer and the R_p layer. Such defects may enhance the transfer of oxygen from the R_p layer toward the CL layer. The mobility of oxygen atoms along a dislocation is enhanced. Dislocations may serve as a fast diffusion channel for oxygen from the R_p region to the unfilled cavities. When the precipitates at R_p are completely dissolved, the dislocations are annihilated.

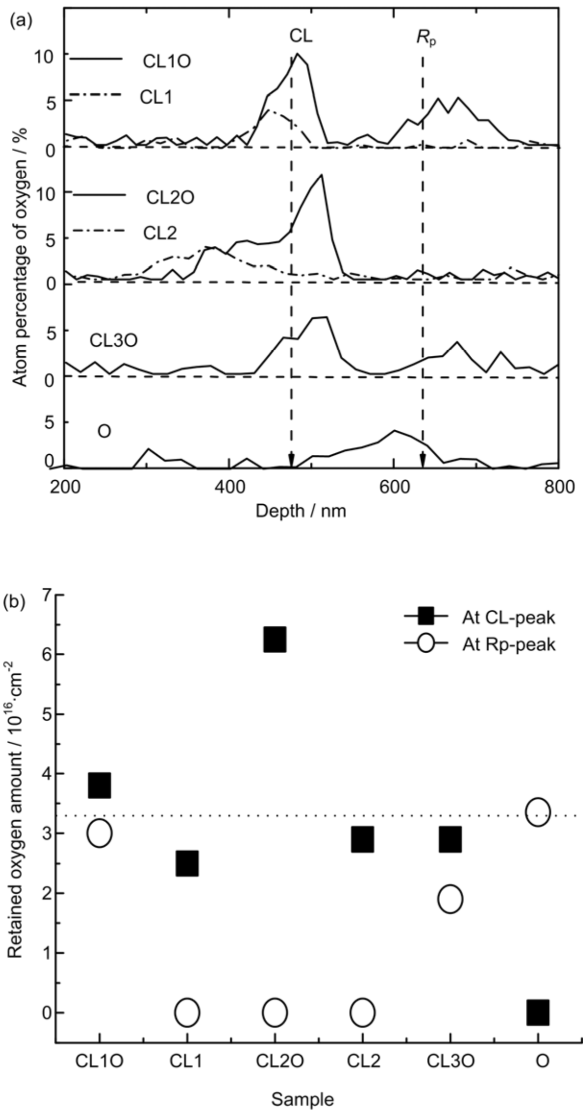

Fig.2 (a)AES profiles of the oxygen distributions in the cavity layer in samples annealed at 1300℃ for 3 hours in an atmosphere of Ar:O_2=100:20. Samples CL1 and CL2 have only cavity layer inside before the annealing (dash and dot line). The depth of the cavity layer (CL) and the R_p of 200 keV O^+ implantation are indicated. (b) Retained amount of the oxygen accumulated at the depth of CL-peak and the R_p-peak of the oxygen profiles. The oxygen dose retained in Sample O (without cavity inside) is indicated by the dashed line.

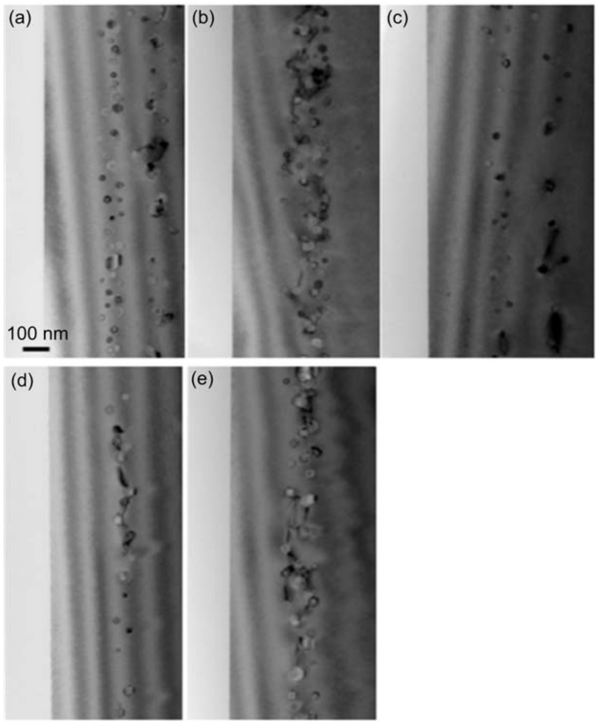

Fig.3 XTEM images showing the distribution of SiO_2 precipitates in CL1O (a), CL2O (b), CL3O (c), CL1 (d) and CL2 (e).

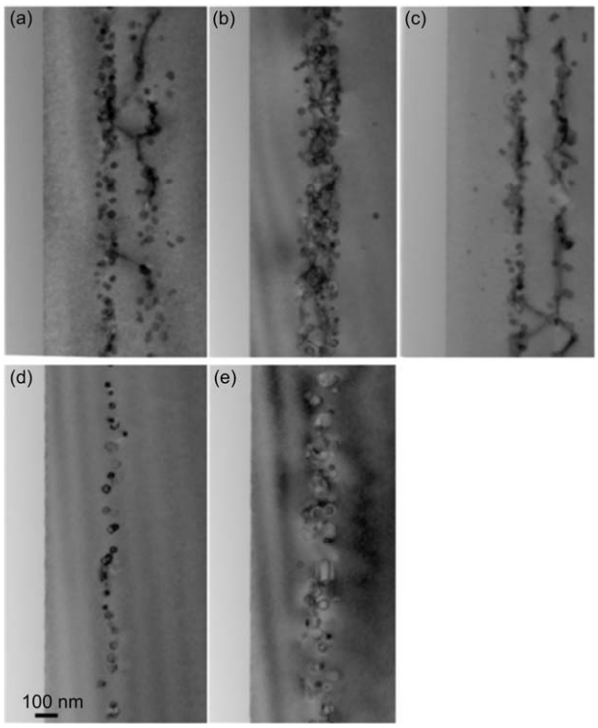

Fig.4 XTEM images of the thick area of the XTEM species, showing the dislocation among the SiO_2 precipitates in Samples CL1O (a), CL2O (b), CL3O (c), CL1 (d) and CL2 (e).

From these results it can be concluded that the cavity layer exhibits much stronger oxygen gettering ability than that of the buried SiO_2 precipitates and the

He dose is a key parameter to enhance the oxygen gettering ability during the high temperature oxidation process. After the internal wall of a pre-formed cavity is covered by one layer of SiO_2, the faceted interface of Si substrate/SiO_2 is still an efficient oxygen gettering site, because the empty volume remained in the cavity may accommodate the released Si interstitials induced by the oxidation process.

On one hand, the oxidation of Si is accompanied by volume expansion and an ejection of Si interstitials suppresses the precipitate growth by inducing a tensile stress surrounding. On the other hand, the oxygen concentration in the superficial Si layer, which controls the incorporation of atmospheric oxygen, may be increased due to presence of the He-induced vacancy-type defect. However, the empty volume in the cavities tends to vanish during the high temperature annealing due to continued volume expansion of SiO_2 formed inside and to the relaxation of Si lattice. The obvious dissolution of a cavity layer formed in Si was detected at around 1100℃ as labelled by the decreasing of empty volume[13]. Considering the cavity layers of Samples CL1, CL2 and CL3 in Fig.1, the distinguished characteristic of the cavity layer in Sample CL2 (Fig.1d) is the large fraction of the cavities in diameters of above 20 nm.

Fig.5 shows a faceted cavity with a SiO_2 layer formed at the internal wall in Sample CL2O. The diameter of the unfilled cavity is as large as 50 nm, which is corresponding to the largest cavity in Fig.1d. This indicates that after annealing at 1300℃, the oxygen gettering effect of a super large cavity is still active. The gettering ability of this sample is not yet saturated. The retained empty volume is sufficient for a long lasting oxygen gettering effect also during high temperature oxidation. In Sample CL2O, the relatively smaller SiO_2 precipitates formed at R_p was dissolved during the high temperature treatment.

The dislocation evolution in the usual SIMOX sample has been demonstrated by Nakashima *et al*[14]. There is a critical size of a SiO_2 precipitate above which a dislocation is generated at the interface of Si/SiO_2 precipitates and grows into a threading dislocation. Below the critical size of the oxide precipitate, the dislocation is unstable and tends to transform to a strain field[15]. In our process dislocations are only found among the SiO_2 precipitates at R_p (Fig.4) or pined between the precipitates at cavity layer and at the R_p region. The region among the precipitates formed in the cavity layer is almost dislocation free. This observation is attributed to the fact that the free volume in this region leads to Si interstitial annihilation and strains relaxation and therefore, the sizes of precipitates formed there are below the critical sizes to generate dislocations[16].

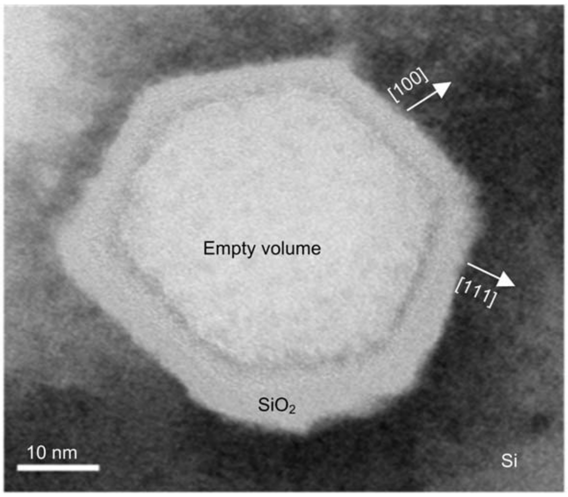

Fig.5 XTEM image showing the unfilled cavity in Sample CL2O annealed at 1300℃ for 3 h in an atmosphere of Ar:O_2=100:20.

In conclusion, a cavity layer induced by He implantation and annealing before oxygen implantation is an efficient gettering layer for oxygen and initiates the in-diffusion of oxygen from the atmosphere into the superficial Si layer during the high temperature oxidation process. The gettering ability of the cavity layer can be enhanced by increasing the mean size of cavities *via* increasing the He ion dose. The implanted oxygen is redistributed from the R_p region into the cavity layer as far as the oxygen gettering ability of the cavity layer is not saturated yet. Very few dislocations are observed among the SiO_2 precipitates formed in the cavity layer. Such dislocations are frequently found among precipitates formed in the conventional SIMOX process.

References

1 Raineri V, Fallica P G, Percolla G, *et al.* J Appl Phys, 1995, **78:** 3727–3735.

2 Follstaedt D M, Myers S M, Peersen G A, *et al.* J Electron Mater, 1996, **25:** 151–160.

3 Job R, Ulyashin A G, Fahrner W R, *et al.* Appl Phys A, 2001, **7**2: 325–332.
4 Mirabella S, Bruno E, Priolo F, *et al.* Appl Phys Lett 2002, **88**: 191910–191912.
5 Maria J. SIMOX. Anc, published by the institution of Electrical Engineers, Stevenage Herts., UK, ISBN 0 86341 334 X, 2004.
6 Nakashima S, Katayama T, Miyamura Y, *et al.* Proc IEEE SOI Conf, 1994, 17–18.
7 Matsumura A, Hamaguchi I, Kawamura K, *et al.* Microelectron Eng, 2003, **66:** 400–408.
8 Chen M, Wang X, Chen J, *et al.* Appl Phys Lett, 2002, **80:** 880–882.
9 Jiao J, Johnson B, Seraphin S, *et al.* Mater Sci Eng B, 2000, **72:** 150–156.
10 Wong-Leung J, Nygren E, Williams J S, *et al.* Appl Phys Lett, 1995, **67:** 416–418.
11 Biersack J, Haggmark L G. Nucl Instrum Methods B, 1980, **174:** 571–576.
12 Evans J H. Nucl Instrum Methods Phys Res B, 2001, **178:** 33–38.
13 Raineri V, Saggio M, Rimini E, *et al.* J Mater Res, 2000, **15:** 1449–1454.
14 Nakashima S, Izumi K. J Mater Res, 1993, **8:** 523–533.
15 Ashby M F, Johnson L. Philos Mag, 1969, **20:** 1009–1014.
16 Kalyanaraman R, Haynes T E, Venezia V C, *et al.* Appl Phys Lett, 2000 , **76:** 3379–3381.